

Interaction Energy Surfaces for $\text{Li}(2^2\text{S})$ and $\text{Li}(2^2\text{P})$ With H_2^*

M. Krauss

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

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Interaction energy surfaces for the interaction of $\text{Li}(2^2\text{S})$ and $\text{Li}(2^2\text{P})$ with H_2 are calculated using approximate Hartree-Fock trial functions. The crossing of energy curves is observed for C_{2v} conformations if the H_2 internuclear distance is sufficiently large. No crossing is observed for colinear collisions for any H_2 distance.

The wave function of the strongly attractive state involved in the crossing is related to the metastable negative-ion states that are postulated to account for resonant electron-molecule scattering. Such a charge-transfer state can only be bound for C_{2v} conformations for the H_2 molecule. The likelihood and geometry of the crossing complexes for other molecules interacting with alkalis is discussed in terms of the formation of these resonance charge-transfer states.

Key Words: Energy surface; $\text{Li}(2^2\text{S})$; $\text{Li}(2^2\text{P})$; $\text{H}_2(\text{X}^1\Sigma_g^+)$; Hartree-Fock; energy transfer; resonance state; charge-transfer.

1. Introduction

Fundamental to the understanding of electronic-vibrational energy transfer involving alkali atoms and diatomic molecules is an accurate representation of the energy of interaction. The qualitative features of these surfaces was first considered with semi-empirical techniques [1].¹ To this date there are no ab initio calculations. Accurate energy calculations utilizing correlated wave functions are not yet possible but these systems can be investigated immediately with available Hartree-Fock (H.F.) programs [2]. This is of value for two reasons. First, the approximate H.F. energy surface is considerably more reliable than the earlier results to the extent that the qualitative features of the surfaces can be fixed. In particular, the question of the angular distribution of the interaction energy can be settled and an estimate given of the activation energy, if any, of the excitation of alkali D radiation by vibrationally excited diatomics. Second, the molecular orbital description is more natural to the discussion of these reactions in the light of recent studies of electron-diatom molecule resonant scattering [3].

This note will examine the qualitative behavior of the $\text{Li}(2^2\text{S})$ and $\text{Li}(2^2\text{P})$ interaction with the H_2 molecule without chemical reaction as the simplest example of the alkali-diatom system. There is a

total of four curves, two repulsive ones, and one weakly, and one strongly attractive curve which are depicted in figure 1. Except for the strongly attractive state there is little overlap of the alkali and diatomic charge distributions. It is our contention that the H.F. surfaces are qualitatively correct and of semiquantitative accuracy for this type of surface. The near constancy of the correlation energy over a wide range of geometries is presumed here [4].

The correlation situation is quite different for the strongly attractive curve. This curve has long been characterized as a charge transfer state [1]. The H.F. function does, in fact, describe a charge transfer state and is related to the ionic valence bond configurations. The negative ion H_2^- state formed here is also related to the lowest energy resonance state of H_2^- considered responsible for enhanced vibrational excitation at low incident electron energies [3]. Three electrons are now interpenetrating and the correlation [5] is similar to that in He_2^+ and H_3 . However, there are offsetting H.F. and correlation errors that are strongly dependent on the geometry. The depth of the H.F. attractive well should approximate the correlated one.

Since even an accurate H.F. calculation of the strongly attractive curve can only be considered qualitative, we have contented ourselves with self-consistent-field solutions far from the H.F. limit. More accurate solutions will be considered when they are needed as a base for a correlated calculation. The H.F. techniques are briefly described and the results for a rather small but meaningful basis are

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¹ Figures in brackets indicate the literature references at the end of this paper.

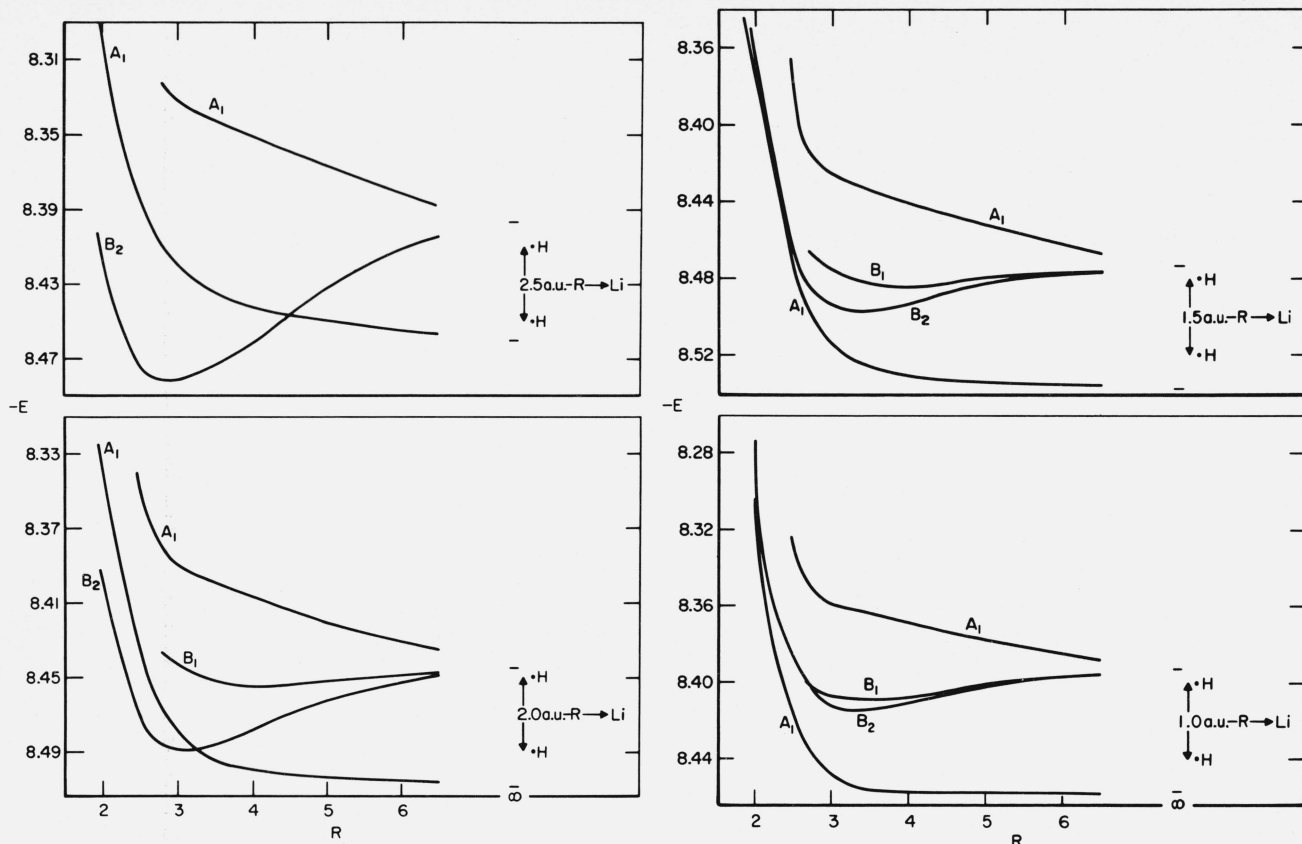


FIGURE 1a. Interaction energies for Li(2S and 2P) with the ground state of H_2 for C_{2v} geometries as a function of the H_2 internuclear distance.
Energies in a.u.

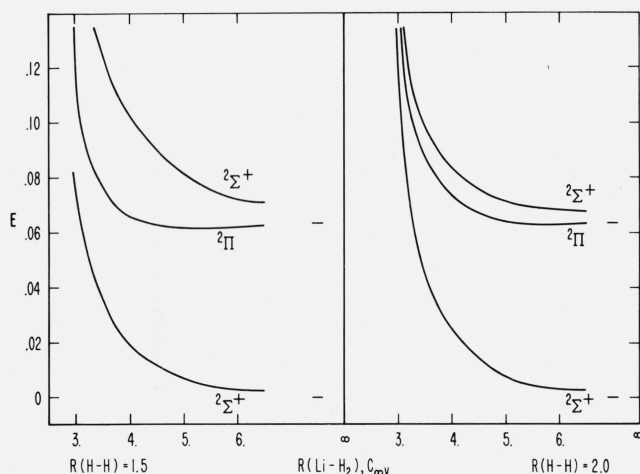


FIGURE 1b. Interaction energies for Li(2S and 2P) with the ground state of H_2 for C_{xv} geometries as a function of the H_2 internuclear distance
Energies in a.u.

given in the next section. Similar calculations were completed for the isoelectronic LiHe system at the same level of accuracy. This permits some calibration

of the approximate H.F. values since limited configuration interaction results [6] exist for LiHe.

In the final section the H.F. results are compared to the earlier semiempirical calculations. The angular distribution and the position of the crossing in the interaction curves are particularly examined and earlier deductions on the linear surface are questioned. Comparison of the H.F. wave functions for the charge-transfer state to the assumed resonance states in electron scattering is pursued to the point of speculation with regard to other systems.

2. Hartree-Fock Calculation

For doublet systems with one open-shell orbital outside of a closed shell core, the H.F. solutions satisfy a variant of the Brillouin theorem that was noted by Davidson [7]. If the vectors are designated $C_{i,\alpha}$ where α designates the open-shell vector for which self-consistency is achieved then

$$C_{i,\alpha} S C_{j,\alpha} = \delta_{ij}$$

and

$$\langle \Psi_{i,\alpha} | H | \Psi_{j,\alpha} \rangle = E_i \delta_{ij}$$

where S is the basis function overlap matrix and H is the total electronic Hamiltonian. $\Psi_{i,\alpha}$ is the H.F. function where the excited φ_i orbital replaces the φ_α orbital in $\Psi_{\alpha,\alpha}$. Calculation of any one state will yield upper bounds to higher Rydberg states. The accuracy of the bounds depends upon the size of the basis set and its ability to fit the higher Rydbergs and the extent to which the core orbitals relax for different $\Psi_{\alpha,\alpha}$. As noted in the introduction no special effort will be made to achieve the H.F. limit. But a reasonably large set must be used to insure correct qualitative behavior. Both the $\text{Li}(2S)$ and $\text{H}(2S)$ bases are chosen from the smallest of the accurate Gaussian-type functions (GTF) sets given by Huzinaga [8]. The $2s_{\text{H}}$, $2p_{\text{Li}}$, $2p_{\text{H}}$, $3s_{\text{Li}}$, and $3p_{\text{Li}}$ orbitals are approximated by choosing effective Slater exponents for the appropriate atomic Rydberg orbitals and using the large coefficient Gaussian fits to the Slater orbitals [9]. This procedure is very rough since not all the GTF required can be used because of computer time limitations so that compromise exponents must be chosen. This set has been contracted severely with the resultant H_2 and Li energies in table 1. The $\text{Li}(2S,2P)$ interval is 0.11 eV larger than the H.F. value and 0.12 eV larger than the experimental value [10]. The error is almost entirely in the $2s_{\text{Li}}$ due to the use of $1s_{\text{Li}}$ coefficients to severely contract the s_{Li} set. For H_2 the error in the H.F. energy is about 0.6 eV at 1.5 a.u. compared to an accurate H.F. energy. This large discrepancy is due to the contraction of the H_2 basis using the Huzinaga expansion coefficients without scaling the orbital exponents. Since the contracted function is equivalent to a single Slater-type function (STF) the $1s$ function exponents determined by Fraga and Ransil [11] can be used as a guide. The larger exponent would improve the energy significantly but would effect improvements mainly in the H_2 binding and not in the interaction-region between the Li and H_2 which is the main concern here. More flexible bases will be used when the correlation is calculated in subsequent work. The errors due to the small basis considerably exceed those that arise from the use of orbital energies to compute the total energies. The general shapes

of all curves can be found in figure 1 for the neutral states and in figure 2 for the $\text{Li}^+ + \text{H}_2$ interaction.

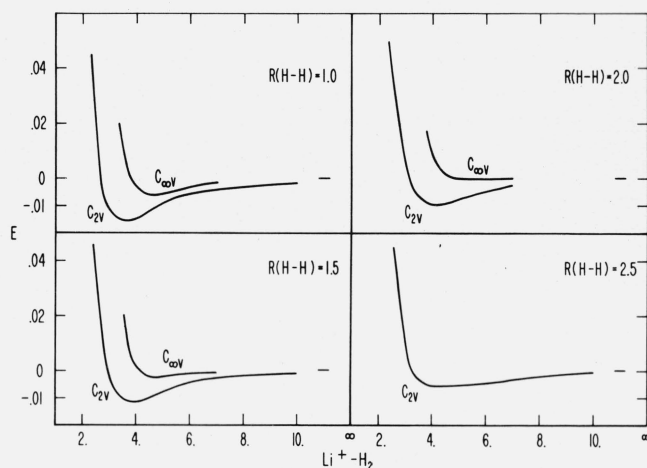


FIGURE 2. Interaction energies for $\text{Li}^+(1S)$ with the ground state of H_2 for (a) C_{2v} and (b) C_{2v} geometries as a function of the H_2 internuclear distance.

Energies in a.u.

The quantitative value of the B_2 curves is limited by an uncertain correlation error. Correlation effects will be considered in two categories. The first type are terms which correlate the asymptotic fragments. The K shell of the Li atom is, of course, essentially unaffected by the interaction. It is presumed that for all but the B_2 state the correlation of the H_2 bond is only slightly changed for moderate interaction energies. The correlation energy curve for H_2 is quite constant at about 1.5 a.u. and then starts to rise rapidly [14]. For the B_2 state the separation of the two hydrogen atoms in the presence of the Li atom does not lead to a large increase in the correlation energy as $R(\text{H}-\text{H})$ exceeds 1.5 a.u. Since a $b_2(1\sigma_u)$ orbital is occupied, the asymptotic fragments would be $\text{H} + \text{H}^+$ with Li^+ for electrical neutrality. The correlation energy [15] for H^+ is only a little less than that for H_2 and the usual large asymptotic correlation error is avoided. For H_2 separations less than about 1.5 a.u. the correlation energy in the H_2 pair should be comparable for the A_1 , B_1 , and B_2 states.

At $R(\text{H}-\text{H}) = 2.5$ a.u. the B_2 state would be about 0.01 a.u. lower in energy than the A_1 and B_1 states due to the difference in correlation energy in the H_2 electron-pair for the two categories of states. Offsetting this error would be the increase in the second category of the correlation energy due to the three interpenetrating electrons in the B_2 state. For He_2^+ the correlation energy at equilibrium exceeds that for the He atom by about 0.025 a.u. It is not expected that the additional correlation energy in LiH_2 2B_2 will be that large since the charge is not completely transferred from the Li atom in the range of conformations of interest. Assuming a direct proportionality of the excess correlation energy to the

TABLE 1. Energies of asymptotic atoms and molecule

Atom/molecule	-E ^a	
	Present calculation	Accurate H.F.
He	2.86113	^b 2.86168
Li ⁺	7.23597	^b 7.23641
Li(² S)	7.42714	^c 7.432724
Li(² P)	7.36342	^c 7.365068
H ₂ (1.0) ^d	1.02984	
H ₂ (1.5)	1.11010	
H ₂ (2.0)	1.08197	
H ₂ (2.5)	1.03299	
H ₂ (1.4)		^e 1.13354

^a Energy in atomic units: a.u. of energy = $e^2/a_0 = 27.210$ eV.

^b T. Gilbert and P. Bagus, unpublished results.

^c A. W. Weiss, *Astrophys. J.* **138**, 1262 (1963).

^d $H_2(R)$ where the distance R is in atomic units: 1 a.u. of length = $a_0 = 0.52793 \cdot 10^{-8}$ cm.

^e W. Kolos and C. C. J. Roothan, *Revs. Modern Phys.* **32**, 205 (1960).

amount of charge transferred, the value is 0.008 a.u. for the curve where $R(\text{H}-\text{H})$ is 1.5 a.u. On this basis it is felt that the calculated surfaces are semiquantitatively correct. For these surfaces the zero activation energy crossing for activation of the ^2P state by colliding the ^2S atom with a vibrationally excited molecule occurs at a conformation where $R(\text{H}-\text{H})$ is a little less than 2.0 a.u.

An oblique check on these calculations can also be made by considering the isoelectronic diatomic interaction $\text{Li}+\text{He}$ for which accurate calculations exist. The asymptotic error is still due to the poor $\text{Li}(^2\text{S})$ function. Only the $^2\Pi$ state was calculated directly and the well depth and spectroscopic constants for the $^2\Pi$ states are compared in table 2. All the LiHe interaction energy curves are exhibited in figure 3.

TABLE 2. Spectroscopic constants and dissociation energy, LiHe

Molecular state	$^2\Pi$	
	This work	Ref. [6]
$D_e(\text{eV})$	0.037	0.06267
$r_e(10^{-8}\text{cm})$	2.04	1.964
$\omega_e(\text{cm}^{-1})$	261.9	285.7
$\omega_e x_e(\text{cm}^{-1})$	28.66	39.68
$\alpha_e(\text{cm}^{-1})$	0.144	0.183

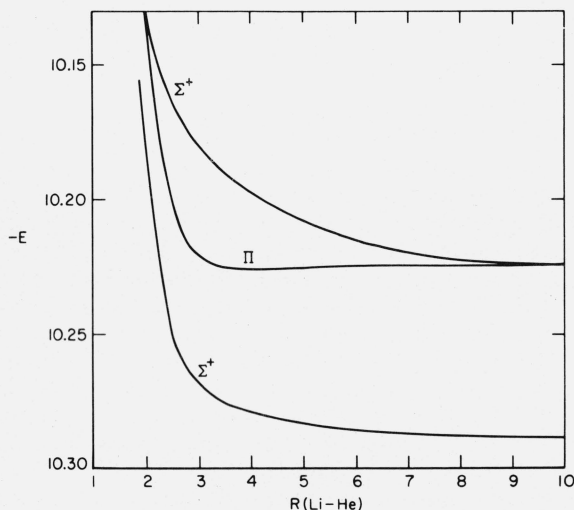


FIGURE 3. Interaction energies for $\text{Li}(^2\text{S}$ and $^2\text{P})$ with the ground state of He . Energies in a.u.

3. Discussion

The present results confirm the early Heitler-London predictions of crossings in the energy curves for triangular geometries [1a]. There are no crossings in the colinear cases. In fact the linear curves strongly resemble the LiHe interaction energy curve. Laidler [1b] has discussed the $\text{Na}(^2\text{P})$ quenching in terms of the linear complex and has

argued that the conclusions would not be affected by the shape of the complex. For the Li reactions the portion of the surface calculated here would argue quite the opposite. It is improbable that colinear collisions of vibrationally excited or dissociated H_2 with $\text{Li}(^2\text{S})$ would lead to excitation to $\text{Li}(^2\text{P})$ or the converse. But crossings are available in the C_{2v} configuration and there is no classical activation energy. The curves indicate a very rapid change in crossing position and well depth as a function of the internuclear H_2 distance. This would permit the strong coupling of the electronic and vibrational degrees of freedom which is in accord with both past [1b] and present [12] interpretations of these reactions. In particular deactivation of alkali resonance radiation will occur predominantly by vibrational excitation.

Two features of the curves are worth special mention. First, the crossing in the Hartree-Fock approximation is a kind of conical intersection [13] of energy curves. The doublet open-shell configurations have all off-diagonal energy matrix elements zero even if the symmetries are identical. $^2\text{A}'$ states would exhibit a conical intersection in the H.F. approximation. However, it is difficult to see how the degeneracy could be maintained when the full correlation interaction is introduced although the splitting is probably small. The second feature is the almost congruence of the H.F. $^2\text{B}_1$ or $^2\Pi$ neutral curves and the ion curve for the same geometry. The well depth in the Π -type states is not due, in this approximation, to any slight binding in the π orbital but predominately to the ion core interaction with a polarizable, unshielded atom. Similar results are found for LiHe . Although the well depths are about 40 percent smaller than those of Schneiderman and Michels or an accurate H.F. result, the qualitative behavior is similar. The $^2\Pi$ and $^1\Sigma^+$ well depths are quite comparable with the $^2\Pi$ dissociation energy greater by 0.01 eV.

The large H_2 separations required for the crossing were previously linked to the $^2\Sigma_u^+$ state [1] of H_2^+ . H.F. wave functions can be similarly interpreted. For the B_2 state the p orbital is oriented along the H_2 molecule. As the $\text{Li}(^2\text{P})$ approaches H_2 , a fraction of the charge transfers to the H_2 in a charge distribution very much like that of an isolated $1\sigma_u\text{H}_2$ orbital. This is a penetrating valence orbital with strong antibonding characteristics which determines both the deep well and the large H_2 equilibrium separations. The picture that develops is that of a charge-transfer state arising from a low ionization potential atom and a diatomic molecule that can support a valencelike negative-ion resonance state. Those molecules which have no available low-lying valence-type orbitals will not have deep attractive interactions with excited alkali atoms. In this category would fall the Ne-isoelectronic molecules and saturated hydrocarbons. Quenching cross-sections are small for such molecules [16]. On the other hand the diatomics like N_2 have the π_g and σ_u type valence orbitals available. The Π_g state can arise from a p orbital in a co-

linear collision for an orientation perpendicular to the line of centers. The C_{2v} geometry requires a d orbital on the alkali since the π_g orbital correlates with an A_2 representation. But the σ_u antibonding valence-type orbital plays the same role in N_2 as it does in H_2 . The relative well depths with angular orientation should provide another measure of the kind of one-particle resonance involved in low energy electron excitation of vibrations. Contrary to H_2 there will probably be a crossing for colinear as well as C_{2v} collisions which could, in part, account for the higher N_2 cross section [17]. The character of the negative-ion should change as a function of angle and as a result so should the vibrational-electronic coupling.

4. References

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